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G804/4280

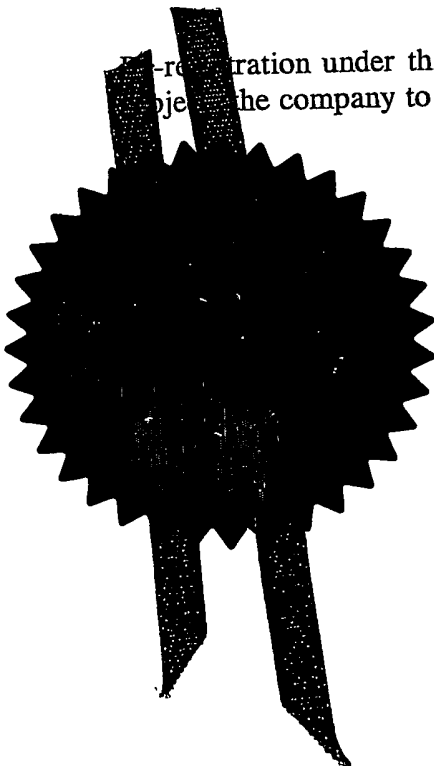
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57.0534 GB NP

2. Patent application number

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3. Full name, address and postcode of the or of each applicant (underline all surnames)

Schlumberger Holdings Limited

PO Box 71
Craigmuir Chambers
Road Town, Tortola
British Virgin Islands

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

British Virgin Islands

7236326001

4. Title of the invention

VISCOELASTIC SURFACTANT GELS WITH REDUCED SALT CONCENTRATION

5. Name of your agent (if you have one)

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

Akram K MIRZA
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Cambridge CB3 0EL
UK

Patents ADP number (if you know it)

4433504002

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Country

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Description 22

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Akram K MIRZA,
01223 325268

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DUPLICATE

VISCOELASTIC SURFACTANT GELS WITH REDUCED SALT CONCENTRATIONField of the Invention

The present invention relates to the use of organic compounds for raising the viscosities and/or reducing the salt requirements of viscoelastic surfactant (VES) gels, and particularly organic compounds having one or more alcohol or amine groups and compositions derived therefrom.

Background of the Invention

In the recovery of hydrocarbons, such as oil and gas, from natural hydrocarbon reservoirs, extensive use is made of wellbore treatment fluids such as drilling fluids, completion fluids, work over fluids, packer fluids, fracturing fluids, diverting fluids, acidising fluids, conformance or permeability control fluids and the like.

In many cases significant components of wellbore fluids are thickening agents, usually based on polymers or viscoelastic surfactants, which serve to control the viscosity of the fluids. Typical viscoelastic surfactants are *N*-erucyl-*N,N*-bis(2-hydroxyethyl)-*N*-methyl ammonium chloride (known as EHAC) and potassium oleate, solutions of which form gels that are responsive to oil when mixed with aqueous brine.

The application of viscoelastic surfactants in both non-foamed and foamed fluids used for fracturing subterranean formations has been described in several patents, e.g. EP-A-0835983, US-5258137, US-5551516, US-5964295 and US-5979557.

The use of viscoelastic surfactants for water shut off treatments is discussed in GB-A-2332224 and for selective acidizing in US 5,979,557 and Chang F.F., Love T., Affeld C.J., Blevins J.B., Thomas R.L. and Fu D.K., "Case study of a novel acid diversion technique in carbonate reservoirs", Society of Petroleum Engineers, 56529, (1999).

The salt concentration required to form the VES gels is typically between 3 and 12 weight percent. Figure 1 shows the measured rheological profiles of two VES gels based on EHAC and potassium oleate. The salt concentrations required for these systems are between 3 to 4 wt% and 6 to 8 wt%, respectively.

A general feature of VES gels is that the viscosity of the gel decreases with increasing temperature. In many cases the viscosity of the gel will show a decrease above a critical temperature. This effect can be clearly seen in Figure 1 where the viscosities of the gels decrease suddenly above about 60°C. In many hydrocarbon well applications, the downhole temperature can be above this critical temperature. When this happens, the performance of a treatment fluid based on the VES gel can be impaired.

Better performance can sometimes be achieved by increasing the brine concentration. But the transportation and handling of large volumes of salts for oilfield applications results in increased operational costs and potential health and safety implications. Due to these operational considerations, VES gels with a salt concentration of over 6% are rarely prepared in the field.

It is known in the art that the addition of an organic salt (often termed a co-surfactant), as opposed to the more common inorganic salt (such as KCl), to a surfactant can produce a VES gel at a lower concentration of added salt. However, these organic-salt gel systems can have little or no tolerance of the introduction of any other type of salt. This often results in the formation of a precipitate or phase separation in use which limits the operational effectiveness of these systems. A review of organic-salt VES systems has been published by Hoffmann and Ebert [Angew. Chem. Int. Ed. Engl., 27, 902-912 (1988)].

The use of long-chain alcohols in conjunction with surfactants has been reported in the literature. A cubic phase of vesicles was formed when octanol and sodium oleate were mixed in water with a relative ratio of 2:1 (see Gradzielski, M., Bergmeier, M., Muller, M., and Hoffmann, H. "Novel gel phase: A cubic phase of densely packed monodisperse, unilamellar vesicles", *J. Phys. Chem.*, 101, 1719 (1997)). However, this is not of a worm-like micellar type gel and is not as responsive to hydrocarbons. The gel formed from cetyl pyridinium chloride and NaCl is weakened upon the addition of 4-propyl phenol and further addition of the alcohol results in phase separation (see Rehage, H. and Hoffmann, H., "Viscoelastic surfactant solutions: model systems for rheological research", *Mol. Phys.*, 74, 933 (1991)).

Patist et al. have observed that long-chain alcohols have an effect upon the NMR relaxation time of spherical micelles (Patist, A., Axelberd, T., and Shah, D.O., "Effect of long chain alcohols on micellar relaxation time and foaming properties of sodium dodecyl sulfate", *J. Coll. Int. Sci.*,

208, 259 (1998)). They postulate that the sodium dodecyl sulfate micelles pack more tightly when the alcohol is present.

5 It is also known to dilute VES-based treatment fluids with alcohol (see e.g. US 5,551,516 and US 6,239,183). However, alcohol additions of this type are typically made with the aim of producing a suitable surface viscosity for injection. The effect of such additions on the downhole rheological
10 performance of VES gels has not been investigated.

Furthermore, WO 01/77487 describes the use of an alcohol or amine additive to reduce the viscosity of a viscoelastic surfactant based fluid. As is described therein, above a critical concentration, specific to the alcohol or amine
15 additive, the addition of the alcohol or amine may reduce the viscosity of the gel. This critical alcohol or amine concentration depends on temperature such that typically a lower critical concentration is observed at elevated temperature. In this situation, a precursor is used to
20 slowly release a concentration of the alcohol which is above the critical concentration, thereby reducing the viscosity.

Summary of the Invention

25 The present invention is at least partly based on the discovery that the temperature at which the viscosity of a VES gel decreases can be increased by the addition of an alcohol or amine. We have also discovered that such an addition can cause an increase in the viscosity of the VES
30 gel.

Accordingly, a first aspect of the present invention provides a wellbore fluid and its use including an organic compound

having one or more polar groups to raise the critical temperature of a VES gel useful in a wellbore treatment fluid.

5 Thus the organic compound can be used to extend the range of downhole operating temperatures under which VES gels can be usefully employed.

10 A second aspect of the present invention provides the use of an organic compound having one or more alcohol or amine groups to reduce the concentration of inorganic salt that raises the viscosity of a VES gel above a level useful in a wellbore treatment fluid.

15 In a further embodiment of this aspect of the invention, in a VES gel comprising an inorganic salt, the present invention provides the use of an organic compound having one or more alcohol or amine groups to reduce or substantially eliminate the amount of that salt. The salt concentration of the well
20 bore fluid in wt% preferably ranges between 0 and 6, more preferably between 0 and 4 and even more preferable between 0 and 3, or even under 3 using for example fresh water instead of brine.

25 Advantageously, the organic compound used in this way allows the inorganic salt requirements of VES gels to be reduced. Indeed, under certain circumstances, the useful viscosity level can be achieved in the absence of inorganic salt.

30 Furthermore, the first and second aspects can be combined and an organic compound having one or more alcohol or amine groups can be used to both raise the temperature at which the viscosity of a VES gel falls below a level useful in a

wellbore treatment fluid, and to reduce the concentration of inorganic salt required to raise the viscosity of a VES gel above that level.

5 A further aspect of the present invention provides a method of treating a subterranean formation of a hydrocarbon well comprising injecting a treatment fluid into the well, the fluid comprising a surfactant for forming a VES gel, an organic compound having one or more alcohol or amine groups,
10 and optionally an inorganic salt; whereby the organic compound raises the temperature at which the viscosity of the VES gel falls below a level useful for treating a subterranean formation of a hydrocarbon well, and/or reduces the concentration of inorganic salt required to raise the
15 viscosity of the VES gel above that level.

The wellbore treatment fluid may be e.g. a fracturing fluid, a selective acidising fluid or diverting fluid, or a water shut-off fluid. Fracturing fluids are used to create opening
20 or cracks in the formation and carry components such as proppants to prevent the openings from closing. Diverting fluids are fluids that inhibit access of subsequently injected fluids, such as acidising fluids, into formation layers with low oil saturation.

25 The following optional features and preferred embodiments relate to any of the previous aspects of the invention.

The viscosity level useful for most well bore applications, including for example fracturing fluids, is generally between
30 50 and 100 cP at a shear rate of 100 s^{-1} . Fluids in accordance with the present invention may exhibit viscosities of 50 cP or 60 cP at temperatures above 50 degrees Celsius,

or above 60 degrees Celsius and even above 70 degrees Celsius without increasing the salt level above 6 wt%.

5 The useful viscosity level should be attained at a broad range of reservoir temperatures. Typically reservoir temperatures can range from around 30°C to around 200°C. Using the present invention, the critical temperature before significant loss of viscosity occurs, can be raised to above 100, 130 and even 150 degrees Celsius without turning to high
10 salt concentrations.

15 The low shear viscosity level useful for effective transport of proppant particles is suitably >1000 cP at less than or equal to 1 s^{-1} .

The viscosity level of a diverting gel useful for VES diversion systems is suitably >20 cP at 100 s^{-1} .

20 The viscosity level useful for water control treatments is typically <100 cP at encountered shear rates. The organic compound may be suitably miscible with the VES gel formulation and it is typically non-ionic.

25 The organic compound may be composed of a linear or branched saturated or partially unsaturated carbon chain comprising one or more polar groups, wherein the polar groups are typically $-\text{OH}$, $-\text{SH}$ or $-\text{NH}_2$. As the observed effect becomes more pronounced at high molecular weight, the organic
30 compound may be preferably selected from a range comprising between 7 and 22 carbon atoms or more preferably comprising between 7 and 16 carbon atoms.

The organic compound may contain at least one other group selected from an ether, ketone, amide, ester, phosphate ester or phosphonate ester group.

5 The organic compound may be a mono-alcohol, a diol, an ethoxylated alcohol, ethoxylated amine, alkanolamide or fatty acid ethoxylate, for example propan-2-ol, butanol, octan-1-ol, oleyl alcohol, versatyl alcohol, butanediol, butyl amine, oleyl amine or a dimeric oleyl amine.

10 The VES gel may be formed from a surfactant which is anionic, cationic or zwitterionic, and is, for example, a carboxylate or modified carboxylate, a compound of formula R-X-Y-Z (as hereinafter defined), a quaternary ammonium compound, an alkyl betaine/sulphobetaine or an alkyl amido betaine/sulpho-
15 betaine. Preferably the surfactant is derived from oleic acid, linoleic acid or mixtures thereof, erucic acid, tallow acid, dimeric/trimeric/oligomeric carboxylic acids; or is E1018, oleyl ester succinate, oleyl amide succinate, oleyl sarcosinate or N-erucyl-N,N-bis(2-hydroxyethyl)-N-methyl
20 ammonium chloride.

Preferably, the molar ratio, the ration between the concentration measured in mol/l, of the organic compound to the surfactant on which the VES gel is based is 0.5 or less.
25 More preferably, the molar ratio is in the range of 0.05 to 3, and even more preferably in the range of 0.05 to 2.

Brief Description of the Drawings

30 Figure 1 - Rheological profile as a function of temperature of 4 wt% N-erucyl-N,N-bis(2-hydroxyethyl)-N-methyl-ammoniumchloride (EHAC) and 4 wt% potassium oleate gels with respectively 3 and 8 wt% KCl.

Figure 2 - Rheological profile as a function of temperature of two 4 wt% dimeric surfactant gels with respectively 4 and 8 wt% KCl.

5

Figure 3 - Rheological profile as a function of temperature of two 4 wt% dimeric surfactant gels, both with 4 wt% KCl and one with 0.3 molar ratio of oleyl alcohol.

10

Figure 4 - Rheological profile as a function of temperature of two 4 wt% monomeric amide surfactant gels with and without 0.1 molar ratio of oleyl alcohol.

15

Figure 5 - Rheological profile as a function of temperature of three 4 wt% oleyl sarcosinate gels, one without alcohol, and the other two with respectively 0.3 molar ratio of 1-octanol and 0.15 molar ratio of oleyl alcohol.

20

Figure 6 - Rheological profile as a function of temperature of two 4 wt% oleyl sarcosinate gels with and without 0.1 molar ratio of oleyl amine.

25

Figure 7 - Rheological profile as a function of temperature of four 4 wt% oleic acid dimer (E1018, supplied by Cognis Oleochemicals) gels, three with 6 wt% and one with 8 wt% KCl. Two of the gels with 6 wt% KCl also contain 0.15 molar ratio of respectively oleyl alcohol and 1-octanol.

30

Figure 8 - Low shear viscosity of viscoelastic gels based on 3.375 wt% EHAC with and without 1.125 wt% iso-propanol (IPA) as a function of salt (KCl) concentration and temperature.

Figure 9 - Variation of KCl concentration required to produce an optimum viscosity, against temperature for two VES gels based on 3.375 wt% EHAC with and without the addition of 1.125 wt% IPA.

5

Figure 10 - Viscosity at 80°C as a function of shear rate ($0.1-100\text{s}^{-1}$) of a 4 wt% oleyl ester succinate / 1.5 wt% KCl gel with and without 0.1 molar ratio oleyl alcohol.

10

Figure 11 - Rheological profile as a function of temperature of three gels based on Edenor UKD™ (supplied by Cognis Oleochemicals), one gel containing 2.5 wt% Edenor™ and 3 wt% KCl, another gel containing 2 wt% Edenor™ and 3 wt% KCl and 0.5 wt% oleyl diethanolamide, and the last gel containing 2

15

Detailed Description of the Invention

20

In conventional treatment fluids based on VES gels, the temperature dependence of the viscosity may be controlled to some extent by varying the concentration of salt in the VES gel. Figure 2 (discussed more fully below in relation to Example 1) shows the effect of varying the salt concentration on the rheological properties of a VES gel. It can be seen that raising the salt concentration in the gel increases the critical temperature of the VES gel. However, as illustrated by Figure 8 (discussed more fully below in relation to Example 7), the viscosity tends to drop off beyond a certain salt concentration.

25

30

The viscosity level of a wellbore treatment fluid, and in particular of such a fluid useful for treating a subterranean formation of a hydrocarbon well will depend on the type of

treatment. The viscosity of a VES-based fracturing fluid should be 50-100cP at 100s⁻¹, preferably >75cP at 100s⁻¹. In order to transport proppant particles effectively, the fracturing fluid should also have a much higher low shear viscosity, typically >1000cP at <1s⁻¹. For VES diversion systems, the viscosity of the diverting gel should be greater than about 30cP at 100s⁻¹ and preferably about 50cP at 100s⁻¹. For treatments where the fluid is required to penetrate rock matrix, e.g. water control treatments, then the typical fluid viscosity during injection should be <100cP and preferably <50cP throughout the range of shear rates encountered during placement.

Generally, a VES gel-based fluid will display an optimum salt concentration at which the critical temperature shows a maximum. This optimum salt concentration is often above the 6 wt% commonly achievable in oilfield operations and may, in some cases be above 12 wt%.

In VES gels according to the present invention, the addition of an organic compound such as an alcohol or amine to the VES gel has the effect of increasing the critical temperature of the gel.

Alternatively or additionally the addition of an organic compound such as an alcohol or amine reduces or possibly substantially eliminates the salt requirement of the gel. In many cases this allows gels to be formed with similar viscosities to those achieved with the optimum salt concentration in the absence of the organic compound.

The effects of raising the critical temperature of a VES gel and reducing or substantially eliminating the salt

requirement by addition of an organic compound such as an alcohol or amine extend across a wide range of such organic compounds.

5 As used herein, "critical temperature" means the temperature above which the viscosity of the gel ceases to be useful for a wellbore treatment fluid and in particular for the treatment of a subterranean formation of a well. The critical temperature will vary depending on the exact
10 composition of the VES gel, but can be determined for a particular gel using techniques known and available in the art.

The organic compound is typically a compound which is
15 miscible with the VES gel formulation and which either resides mainly in the continuous aqueous phase of the fluid or at least partially resides within the worm-like micellar phase of the fluid. If the compound is too hydrophobic, then a low molar ratio of the compound will migrate to the
20 interior of the worm-like micelles causing the worm-like micellar structure to be broken resulting in a reduction in the viscosity of the fluid at ambient temperature. Relative to the latter behaviour, the preferred compounds are more hydrophilic such that a molar ratio of the compound to the
25 surfactant <0.5 or preferably <0.3 or more preferably ≤ 0.1 does not cause the worm-like structure of the fluid to break, but rather it enhances the viscosity at elevated temperatures and it also reduces the concentration of inorganic salt which is required to optimize the high temperature tolerance of the
30 gel.

The organic compound is preferably non-ionic. Typically it may be composed mainly of a linear or branched saturated or

partially unsaturated carbon chain with a sufficient number of polar groups to impart a hydrophilic-lipophilic balance (HLB) high enough to render the compound miscible with the aqueous VES gel formulation and high enough such that low molar ratios of the compound do not break the worm-like micellar structure of the VES gel. Typical polar group(s) of the compound are -OH, -SH, -NH₂. The compound may also contain other groups such as ether, ketone, amide, ester, phosphate ester or phosphonate ester groups. Thus, when the compound contains -OH groups, it can be a simple mono-alcohol such as propan-2-ol, butanol, octan-1-ol or oleyl alcohol, an alpha-branched alcohol such as versatyl alcohol, a diol such as butanediol or a more complex molecule such as an ethoxylated alcohol, ethoxylated amine, alkanolamide or fatty acid ethoxylate. Dimeric or oligomeric forms such as a dimeric acid ethoxylate may also be used. When the compound is more hydrophilic and completely miscible with the continuous phase, e.g. propan-2-ol or butanediol, then the compound can be symmetric or asymmetric. When the compound is more hydrophobic, e.g. octan-1-ol or oleyl alcohol, then the compound is asymmetric such that it can penetrate the worm-like micelles. When the compound does not contain -OH groups, it can be an amine such as butyl amine, oleyl amine or a dimeric oleyl amine.

For VES treatment fluids formed with alcohol and amine additives, the concentrations of additive required to elevate the critical temperature are similar. In each case, the molar ratio of the additive to the surfactant which forms the VES gel may be 0.5 or less, and more preferably the molar ratio is in the range from 0.01 and 0.4.

The VES gel may be formed from a surfactant which is anionic, cationic or zwitterionic. Typical anionic viscoelastic surfactants include carboxylates and modified carboxylates where the typical carboxylates can be those derived from
5 oleic acid, linoleic acid, erucic acid, mixtures of oleic and linoleic acid, tallow acid, dimeric/trimeric/oligomeric carboxylic acids and where the modified carboxylates can be ethoxycarboxylates, ester carboxylates or amide carboxylates. Exemplary modified carboxylates include oleyl ester

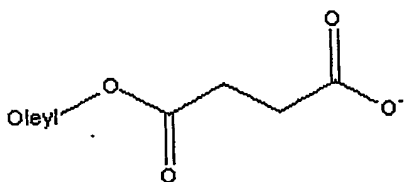
10 ~~succinate, oleyl amide succinate and oleyl sarcosinate.~~ When the viscoelastic surfactant is anionic, it may be of general formula $R-X-Y-Z$ (as described in WO/02/064945 and WO/02/064947) and in which R is the hydrophobic tail of the surfactant, Z is the hydrophilic head of the surfactant, said
15 hydrophilic head group being charged, X is a stabilising group and Y is a linear, saturated or unsaturated chain of 1, 2 or 3 carbon atoms or a branched, saturated or unsaturated hydrocarbon chain wherein the main chain is of 1, 2 or 3 carbon atoms, possibly incorporating an aromatic ring.
20 Preferably the anionic group Z can be carboxylate, COO^- or sulphonate, SO_3^- .

Typical cationic surfactants include quaternary ammonium compounds such as N-erucyl-N,N-bis(2-hydroxy-ethyl)-N-methyl
25 ammonium chloride. Typical zwitterionic surfactants include the alkyl betaines/sulphobetaines and alkyl amido betaines/sulphobetaines where the alkyl group is typically oleyl or erucyl and dimeric/trimeric/oligomeric forms of these betaines/sulphobetaines.

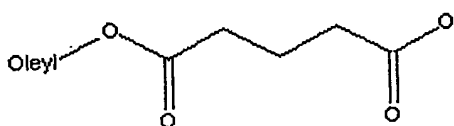
30 Preferred VES surfactants to which the present invention may be applied include conventional commercially available surfactants, such as oleyl ester succinate, oleyl amide

succinate, dimeric oleyl amide succinate, oleyl sarcosinate, oleic acid salt, oleic acid salt dimer, EHAC and a mixture of linoleic and oleic acids, as well as e.g. the surfactant compounds (I-VII) shown below which are intended to have extended temperature capabilities.

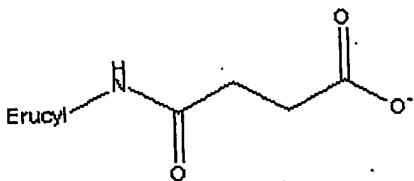
Compound I is oleyl ester succinate (reverse ester bond).
 Compound II is oleyl ester glutarate (reverse ester bond).
 Compound III is erucyl amide succinate (reverse amide bond).
 Compound IV is erucyl amide succinate (forward amide bond).
 Compound V is oleyl amide succinate (reverse amide bond).
 Compound VI is oleyl amide succinate (forward amide bond).
 Compound VII is dimer-(oleyl amide succinate (reverse amide bond)).



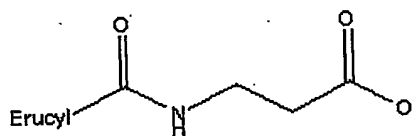
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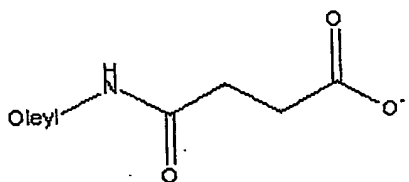
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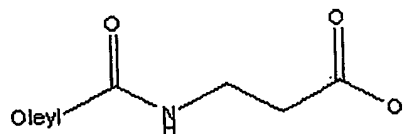
Compound III



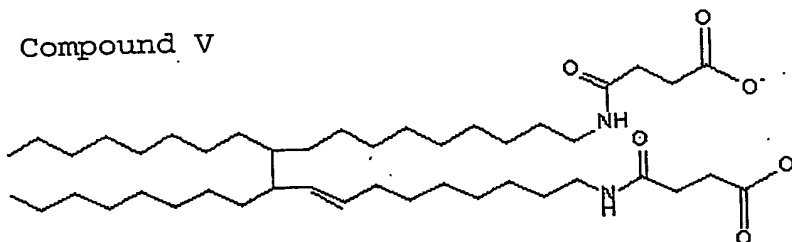
Compound IV



Compound V



Compound VI



Compound VII

VES-based treatment fluids according to the present invention show wide applicability in wellbore applications. The fluids may be used as, for example, fracturing fluids, selective
5 acidising fluids, water shut-off fluids, well clean-out fluids, diversion fluids for acid and scale dissolver treatments. VES-based treatment fluids of the present invention are particularly useful in the treatment of a subterranean formation of a well.

10
VES gel treatment fluids of the present invention may be formulated by simple admixing of the VES surfactant with an appropriate alcohol or amine additive. In some embodiments of the invention, the treatment fluid may also comprise other
15 elements such as a proppant, if the gel is formulated as a fracturing fluid, such as 20-40 mesh sand, bauxite, glass beads etc.

The alcohol or amine additive may be pre-mixed with the
20 surfactant to a given concentration. This facilitates transport of the alcohol or amine additives to oilfield sites. When on site, water or aqueous salt solution (usually KCl brine) is added to the pre-mixed surfactant-alcohol/amine to formulate the treatment fluid.

25
Alternatively, the alcohol or amine additive may be mixed on-site with the surfactant and water/brine to form the treatment fluid.

30 The performance of VES surfactant systems according to the present invention have been assessed in terms of the rheology (variation of viscosity with temperature or salt concentration) of the respective gel.

A controlled stress rheometer (Bohlin model type CVO-50) was used to measure the rheological properties of the solutions. Using a concentric cylinders (Couette) geometry (inner radius of the outer cylinder, $R_i = 1.375$ cm, outer radius of the inner cylinder, $R_o = 1.25$ cm, and inner cylinder length = 3.78 cm), corresponding to the geometry of German DIN standard 53019, the viscosity of each gel was measured at a particular shear rate.

For the particular geometry of the rheometer, the shear rate was calculated as:

$$\dot{\gamma} = \frac{RPM \cdot 2\pi}{60} \frac{2 \cdot R_i^2 R_o^2}{\left(\frac{R_i + R_o}{2}\right)^2 (R_o^2 - R_i^2)}$$

where RPM is the rotational speed (in revolutions per minute) of the inner cylinder. The viscosity was then obtained for each measurement by dividing the measured stress by the calculated shear rate.

Example 1

A surfactant derived from dimeric oleyl amide succinate forms a gel when it is dissolved in aqueous base and salt is added. In a VES gel containing 4 wt% oleyl amide succinate and aqueous KCl, the optimum salt concentration is around 8 wt% KCl. At this salt concentration, the temperature at which the viscosity of the gel drops below 50 cp is just over 130°C. This temperature drops dramatically to just over 70°C if only 4 wt % KCl is added. This effect can be seen in Figure 2. The temperature at which the viscosity of the gel drops below 50 cp is raised when a 0.3 molar ratio of oleyl alcohol is added. This effect can be seen in Figure 3 where the temperature at which the viscosity of the gel drops below

50 cp is approximately 60°C with no alcohol added as compared to approximately 100°C for the gel containing 0.3 molar ratio oleyl alcohol. The gel with 4 wt% KCl and a 0.3 molar ratio of oleyl alcohol performs almost to the level of the optimized system which has 8 wt% KCl as shown in Figure 2. This effect can be used to maintain performance of these VES gels whilst also lowering the salt requirements for their formation to 6 wt% which is achievable in oilfield applications.

Monomeric oleyl amide succinate shows similar behaviour to that of its dimeric counter-part in forming VES gels on addition of aqueous base and a salt. The rheological performance of the monomeric version of oleyl amide succinate is shown in Figure 4. The optimum salt concentration for this VES system is 10 wt% and again, a dramatic loss of performance is observed when the salt concentration is reduced to 4 wt%. Addition of a 0.1 molar ratio of oleyl alcohol increases the temperature at which the system has gel properties, therefore increasing the application range of the material.

Example 2

The method of Example 1 is also applicable to other amide systems, such as oleyl sarcosinate (commercially available from Dow chemicals and known as Hamposyl O). A 4 wt% solution of the amide requires 10 wt% KCl to remain as a gel up to around 100°C. The viscosity of the same material with only 6 wt% KCl loses its gel properties at just under 80°C. The addition of a 0.15 molar ratio of oleyl alcohol to the gel containing 6 wt% KCl restores the temperature at which the viscosity falls below 50 cp to around 95°C. The rheological profile is shown in Figure 5.

This phenomenon is not only related to oleyl alcohol. On addition of a 0.3 molar ratio of 1-octanol to the VES system containing 6 wt% KCl, the temperature at which the viscosity of the gel falls below 50 cp is restored to around 90°C compared to just under 80°C in the absence of 1-octanol. The effect of adding the 1-octanol to the oleyl sarcosinate gel containing 6 wt% KCl is shown in Figure 5.

Furthermore, on addition of a 0.1 molar ratio of oleyl amine to the VES system containing 6 wt% KCl, the temperature at which the viscosity of the gel falls below 50 cp is restored to around 85°C. The rheological profile for this system is shown in Figure 6.

Example 3

VES gels derived from the salts of oleic acid dimers have also been examined. The KCl concentration required to achieve optimum performance for these systems is around 8 wt%. VES gels based on one of these oleic acid dimers, E1018 (supplied by Cognis) is of interest due to its reasonable tolerance to the presence of divalent cations such as calcium. The gel formed from this blend of oligomeric acids (E1018) has an upper operating temperature of around 90°C.

This temperature drops to below 80°C when the KCl concentration is reduced to the 6 wt% which is manageable in the field. However, the temperature at which the viscosity of a gel formed from E1018 with 6 wt% KCl falls below 50 cp can be raised to around 90°C by the addition of a 0.15 molar ratio of an alcohol such as 1-octanol or oleyl alcohol. This effect is shown in the rheological profile of Figure 7.

It can be seen in Figure 7 that the performance of the VES gel formed from E1018 with 6 wt% KCl and 0.15 molar ratio of either oleyl alcohol or 1-octanol is comparable to that of a gel formed from E1018 with 8 wt% KCl. The lowering of the salt requirements to 6 wt% or below makes these gels more practical to use in the field.

Example 4

N-erucyl-*N,N*-bis(2-hydroxyethyl)-*N*-methyllummonium chloride (EHAC) forms VES gels in the presence of chloride salt solutions (see Figure 1). However, the concentration of salt required to form the strongest gel is reduced when isopropanol is added to the system.

A range of VES gels were formulated with 3.375 wt% EHAC and varying overall concentrations of KCl. The viscosity of these gels was tested at each of 40, 60, 80, and 100°C. The results of these tests are shown in Figure 8 as the solid lines of the rheological profiles. It can be seen from Figure 8 that this gel system shows a definite optimum salt concentration which results in the highest viscosity at each temperature tested. For the gels containing only EHAC and KCl, the optimum salt concentration lies between 4 and 6 wt % depending upon the temperature of the gel.

A second range of VES gels was then formulated again with 3.375 wt% EHAC and varying overall concentrations of KCl but now with an additional 1.125 wt% iso-propyl alcohol (IPA). The viscosity of these gels was tested at each of 40, 60, 80, and 100°C. The results of these tests are shown in Figure 8 as the dashed lines of the rheological profiles. It can be seen that in each case, the addition of IPA results in the optimum salt concentration at which the highest viscosity is

achieved being shifted to lower values. In addition, the maximum viscosity achieved at each of the temperatures tested is higher in the gels containing IPA than in those with only EHAC and KCl.

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The effect of adding 1.125 wt% IPA to the 3.375 wt% EHAC solution is shown in Figure 9. From this figure it can be seen that the addition of 1.125 wt% IPA to the EHAC based VES gel results in the lowering of the optimum KCl concentration by between 2 and 2.5 wt%.

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Example 5

Two VES gels were formulated, the first using 4 wt% oleyl ester succinate surfactant and 1.5 wt% KCl and the second the same but including 0.1 molar ratio of oleyl alcohol. The viscosity at 80°C of the gels is shown in Figure 10 as a function of shear rate ($0.1-100\text{s}^{-1}$). It can be seen that the viscosity of the VES gel containing oleyl alcohol is higher than that without the added alcohol with increasing shear rates.

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Example 6

A commercial mixture of linoleic and oleic acids (sold under the name Edenor™) is known to form VES gels on addition of aqueous KCl. Without other additions, around 10 wt% KCl is required to give optimum temperature performance. Figure 11 shows the rheological profile of two Edenor-based VES gels with respectively 3 and 10 wt% KCl added and a further gel which contains 0.5 wt% oleic diethanolamide and 3 wt% KCl. It can be seen in Figure 11 that the viscosity of the VES gel with 10 wt% added KCl drops below the 50 cp threshold at just over 80°C. If the gel contains only 3 wt% KCl, this

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temperature is lowered dramatically to about 35°C. However, when 0.5 wt% oleic diethanolamide is added to the gel with 3 wt% KCl, this temperature recovers to almost the same level as the gel with 10 wt% KCl.

5 While the invention has been described in conjunction with the exemplary embodiments described above, many equivalent modifications and variations will be apparent to those skilled in the art when given this disclosure. Accordingly,
the exemplary embodiments of the invention set forth above
10 are considered to be illustrative and not limiting. Various changes to the described embodiments may be made without departing from the spirit and scope of the invention.

Claims

1. Use of an organic compound having one or more alcohol or amine groups to raise the critical temperature of a viscoelastic surfactant (VES) gel useful in a wellbore treatment fluid.
2. Use of an organic compound having one or more alcohol or amine groups to reduce the concentration of inorganic salt that raises the viscosity of a VES gel above a level useful in a wellbore treatment fluid.
3. Use according to claim 1 or 2, wherein the viscosity level useful for a fracturing fluid is between 50 and 100 cP at a shear rate of 100 s^{-1} .
4. Use according to claim 1 or 2, wherein the low shear viscosity level useful for effective transport of proppant particles is $>1000 \text{ cP}$ at less than or equal to 1 s^{-1} .
5. Use according to claim 1 or 2, wherein the viscosity level of a diverting gel useful for VES diversion systems is $>20 \text{ cP}$ at 100 s^{-1} .
6. Use according to claim 1 or 2, wherein the viscosity level useful for water control treatments is $<100 \text{ cP}$ at encountered shear rates.
7. Use according to any one of the previous claims, wherein the organic compound is miscible with the VES gel formulation.
8. Use according to any one of the previous claims, wherein the organic compound is non-ionic.

9. Use according to claim 8 wherein the organic compound is composed of a linear or branched saturated or partially unsaturated carbon chain comprising one or more polar groups.
- 5 10. Use according to claim 9 wherein the polar groups are - OH, -SH or -NH₂.
11. Use according to claim 10 wherein the compound contains at least one other group selected from an ether, ketone, ~~amide, ester, phosphate ester or phosphonate ester~~
10 group.
12. Use according to any one of claims 7 to 11 wherein the organic compound is a mono-alcohol, a diol, an ethoxylated alcohol, ethoxylated amine, alkanolamide or fatty acid ethoxylate.
- 15 13. Use according to claim 12 wherein the organic compound is propan-2-ol, butanol, octan-1-ol, oleyl alcohol, versatyl alcohol, butanediol, butyl amine, oleyl amine or a dimeric oleyl amine.
- 20 14. Use according to any one of the previous claims, wherein the VES gel is formed from a surfactant which is anionic, cationic or zwitterionic.
- 25 15. Use according to claim 14 wherein the surfactant is a carboxylate or modified carboxylate, a compound of formula R-X-Y-Z (as defined in WO ?? in which R is the hydrophobic tail of the surfactant, Z is the hydrophilic head of the surfactant, preferably carboxylate, COO⁻ or sulphonate, SO₃⁻, said hydrophilic head group being charged, X is a stabilising group and Y is a linear, saturated or unsaturated chain of 1, 2 or 3 carbon atoms
30 or a branched, saturated or unsaturated hydrocarbon

chain wherein the main chain is of 1, 2 or 3 carbon atoms, possibly incorporating an aromatic ring); a quaternary ammonium compound, an alkyl betaine/sulphobetaine or an alkyl amido betaine/sulphobetaine.

16. Use according to claim 15 wherein the surfactant is derived from oleic acid, linoleic acid or mixtures thereof, erucic acid, tallow acid, dimeric/trimeric/oligomeric carboxylic acids; or is El018, oleyl ester succinate, oleyl amide succinate, oleyl sarcosinate or N-erucyl-N,N-bis(2-hydroxyethyl)-N-methyl ammonium chloride.
17. Use according to any one of the previous claims in the treatment of a subterranean formation of a hydrocarbon well.
18. A method of treating a subterranean formation of a hydrocarbon well comprising injecting a treatment fluid into the well, the fluid comprising a surfactant for forming a VES gel, an organic compound having one or more alcohol or amine groups, and optionally an inorganic salt; whereby the organic compound raises the temperature at which the viscosity of the VES gel falls below a level useful for treating a subterranean formation of a hydrocarbon well, and/or reduces the concentration of inorganic salt required to raise the viscosity of the VES gel above that level.
19. A wellbore fluid for injection into subterranean formation, comprising a surfactant for forming a viscoelastic gel; an hydrophilic-lipophilic organic compound with one or more polar groups; and a salt concentration in the range of 0 to 6.0 wt%, wherein the

molar ratio of organic compound to surfactant is in the range of 0.05 to 5 and the viscosity of the fluid at the point of injection is above 20 cp at 100 s⁻¹ at a temperature of above 50 degrees Celsius.

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20. A wellbore diverting fluid for injection into subterranean formation, comprising a surfactant for forming a viscoelastic gel; an hydrophilic-lipophilic organic compound with one or more polar groups; and a salt concentration in the range of 0 to 6.0 wt%, wherein the molar ratio of organic compound to surfactant is in the range of 0.05 to 5 and the viscosity of the fluid at the point of injection is above 20 cp at 100 s⁻¹ at a temperature of above 50 degrees Celsius.

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21. The fluid of claim 19 or claim 20, wherein the salt concentration is less than 5 wt%.

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22. The fluid of claim 19 or claim 20, wherein the salt concentration is less than 3 wt%.

22. The fluid of claim 19 or claim 20, wherein the polar group is selected from -OH, -SH or -NH₂.

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23. The fluid of claim 19, having a viscosity above 50 cp at 100 s⁻¹ at a temperature of above 50 degrees Celsius

24. The fluid of claim 19, having a viscosity above 50 cp at 100 s⁻¹ at a temperature of above 60 degrees Celsius.

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25. The fluid of claim 19, having a viscosity above 60 cp at 100 s⁻¹ at a temperature of above 60 degrees Celsius.

Abstract

5 A well bore treatment fluid of viscoelastic surfactants and methods for increasing the viscosity of the fluid at high temperature without increasing its salt concentration by adding a organic hydrophilic-lipophilic compound having at least one polar group with a molar ratio of 0.05 to 0.5 between the concentration of the compound and the surfactant.

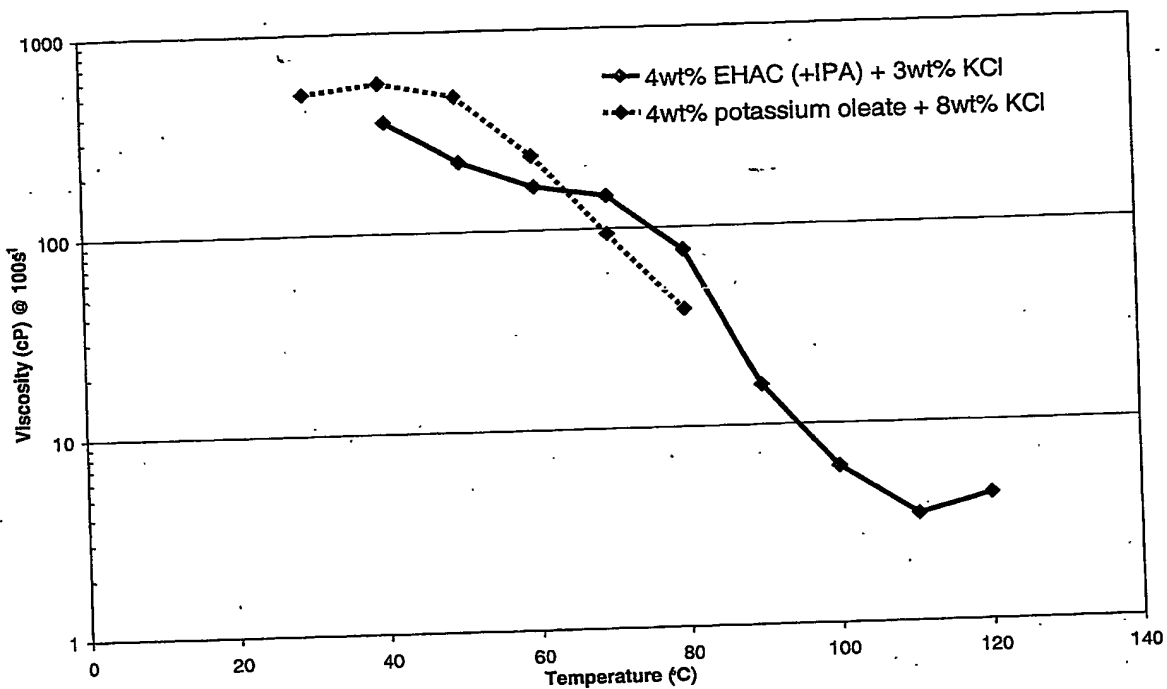


Figure 1

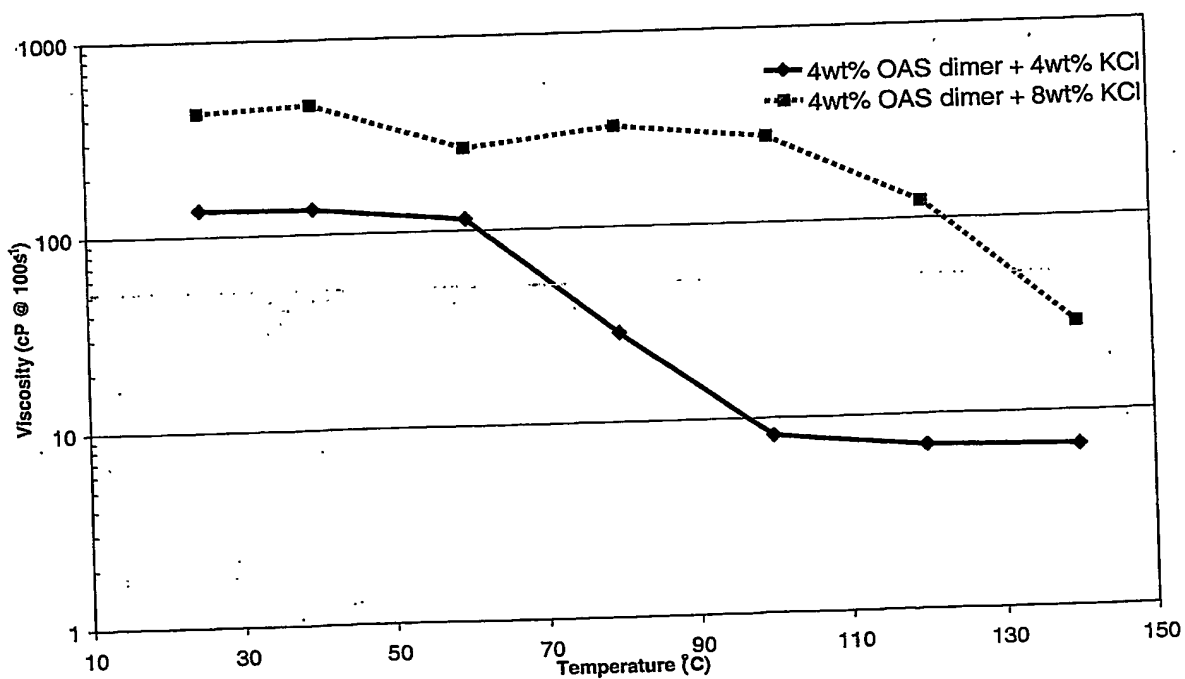


Figure 2

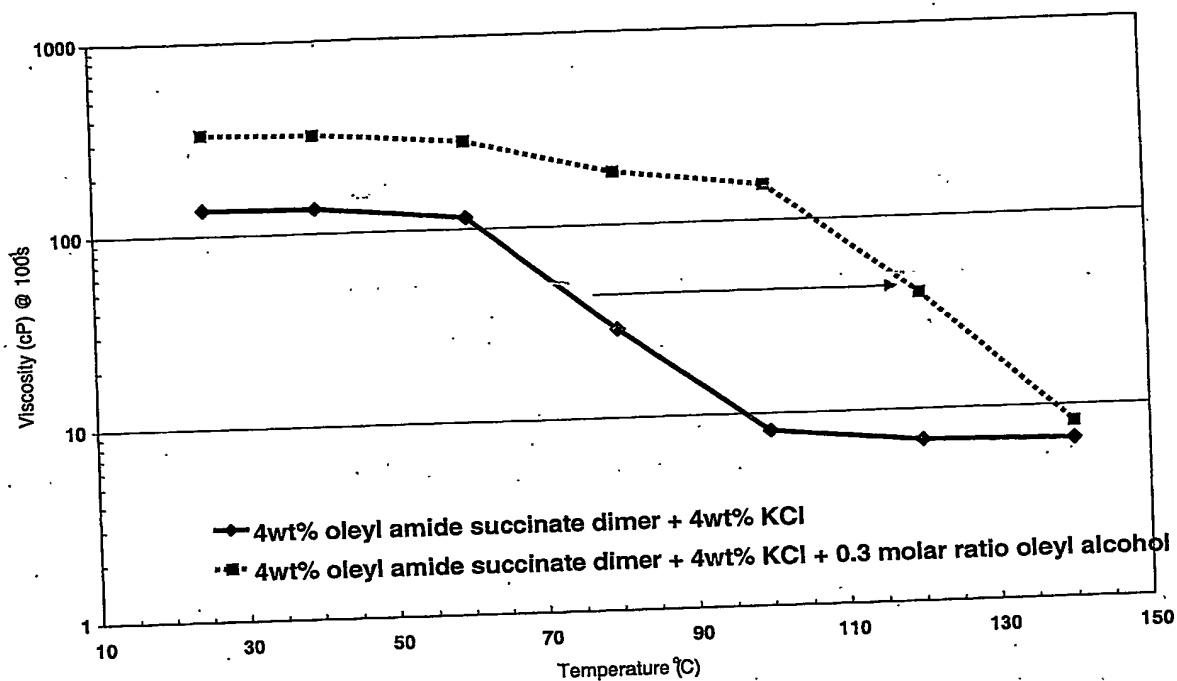


Figure 3

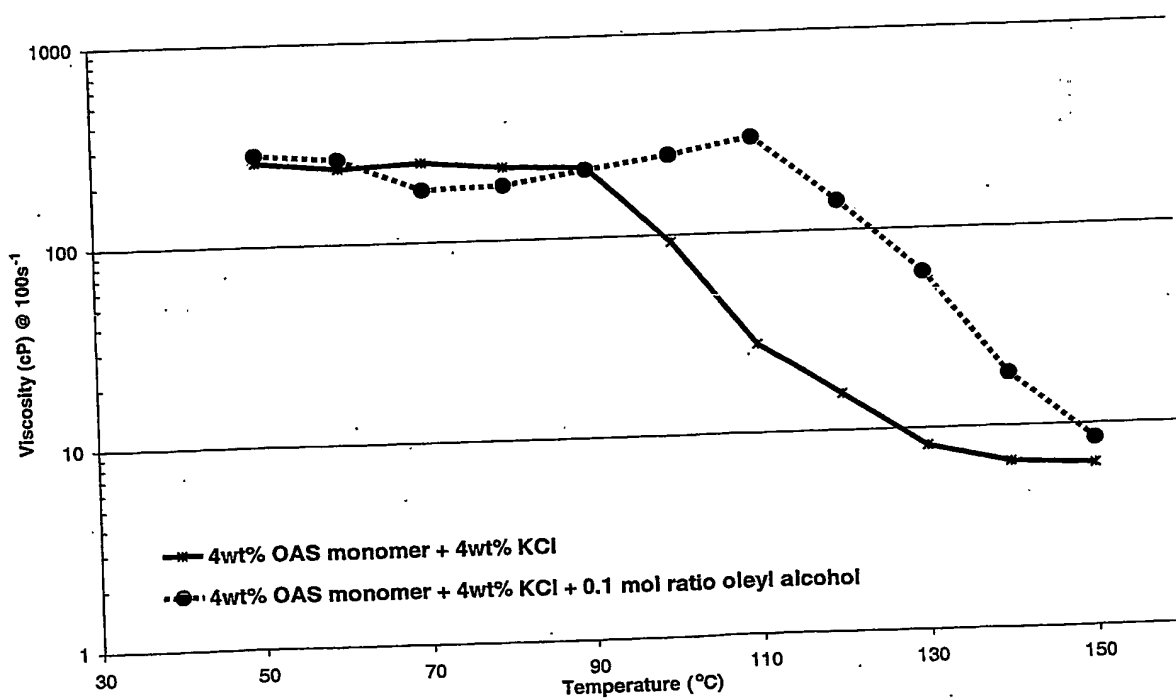


Figure 4

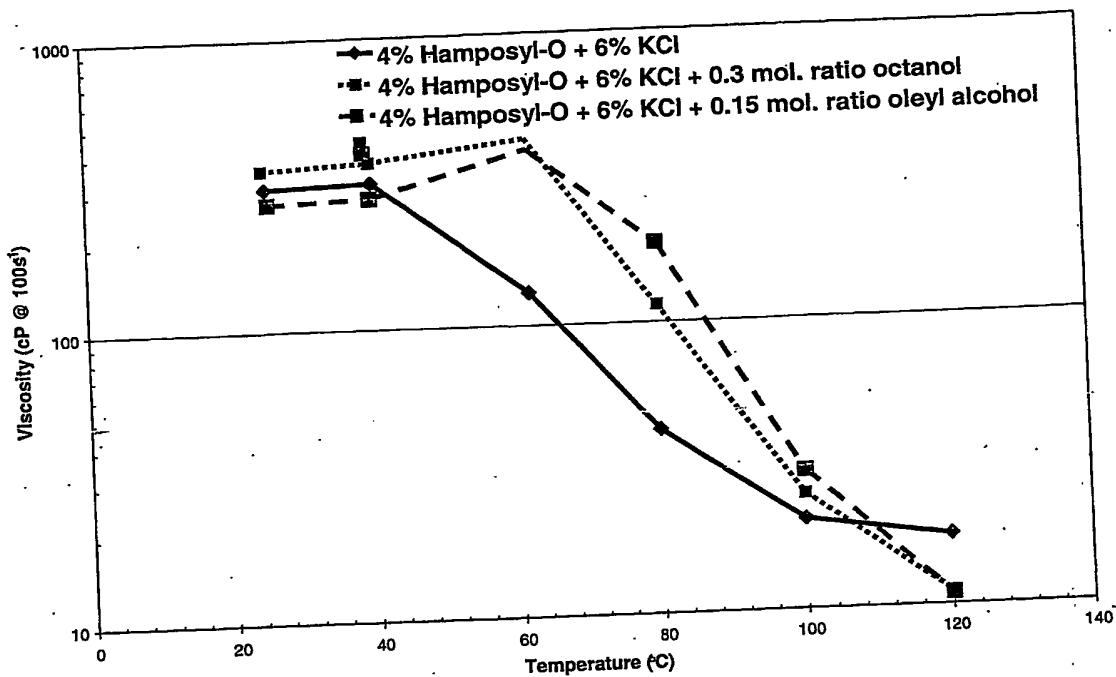


Figure 5

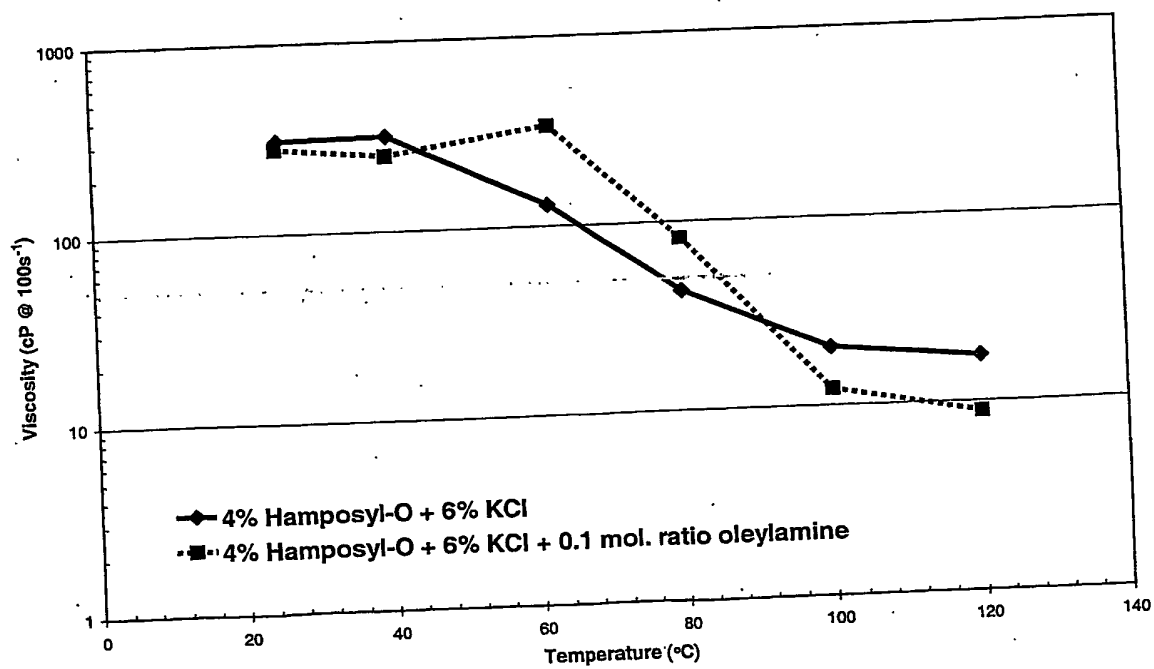


Figure 6

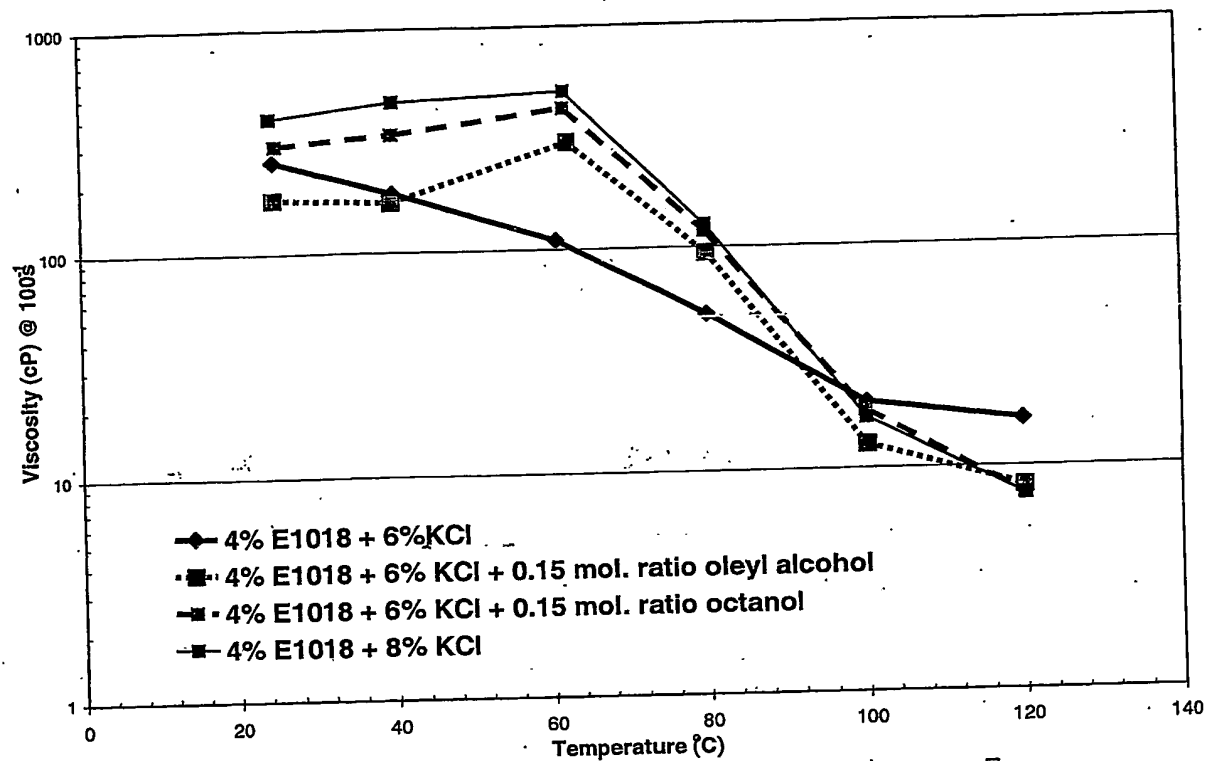


Figure 7

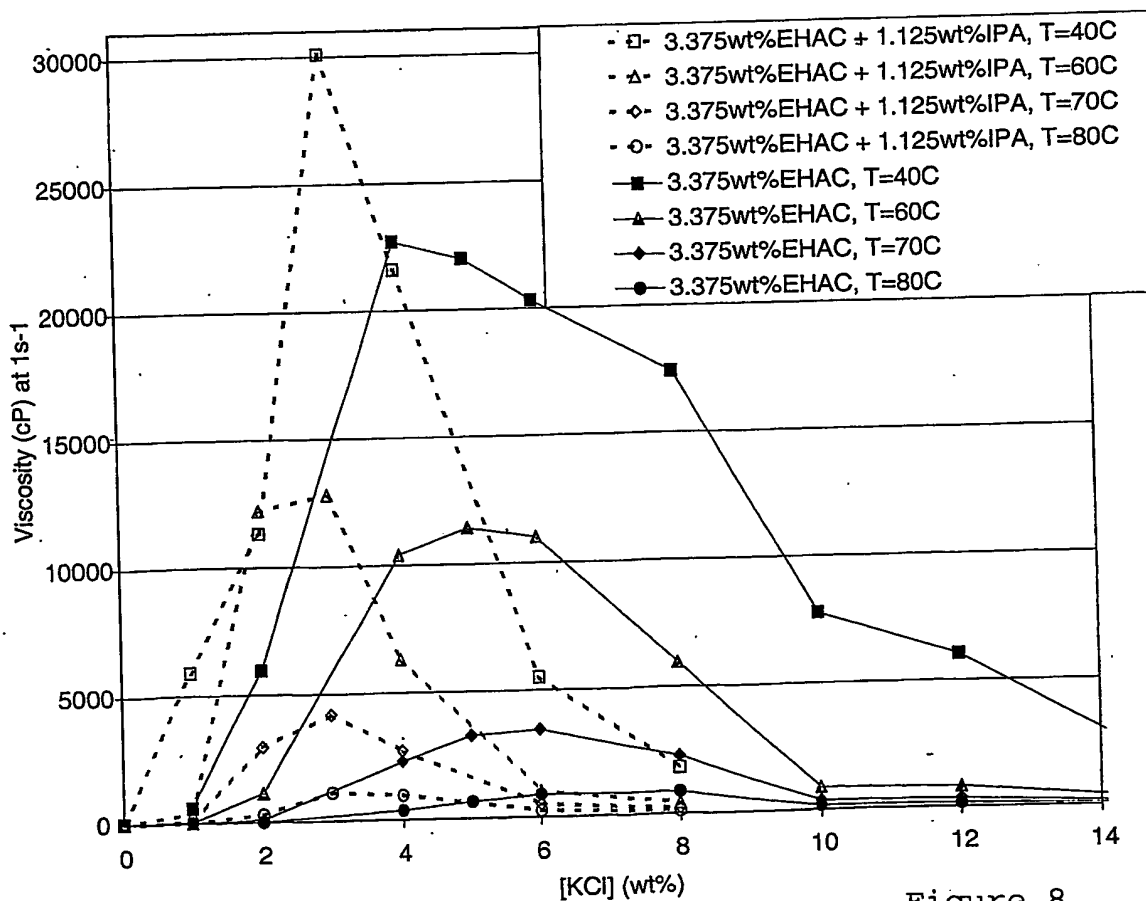


Figure 8

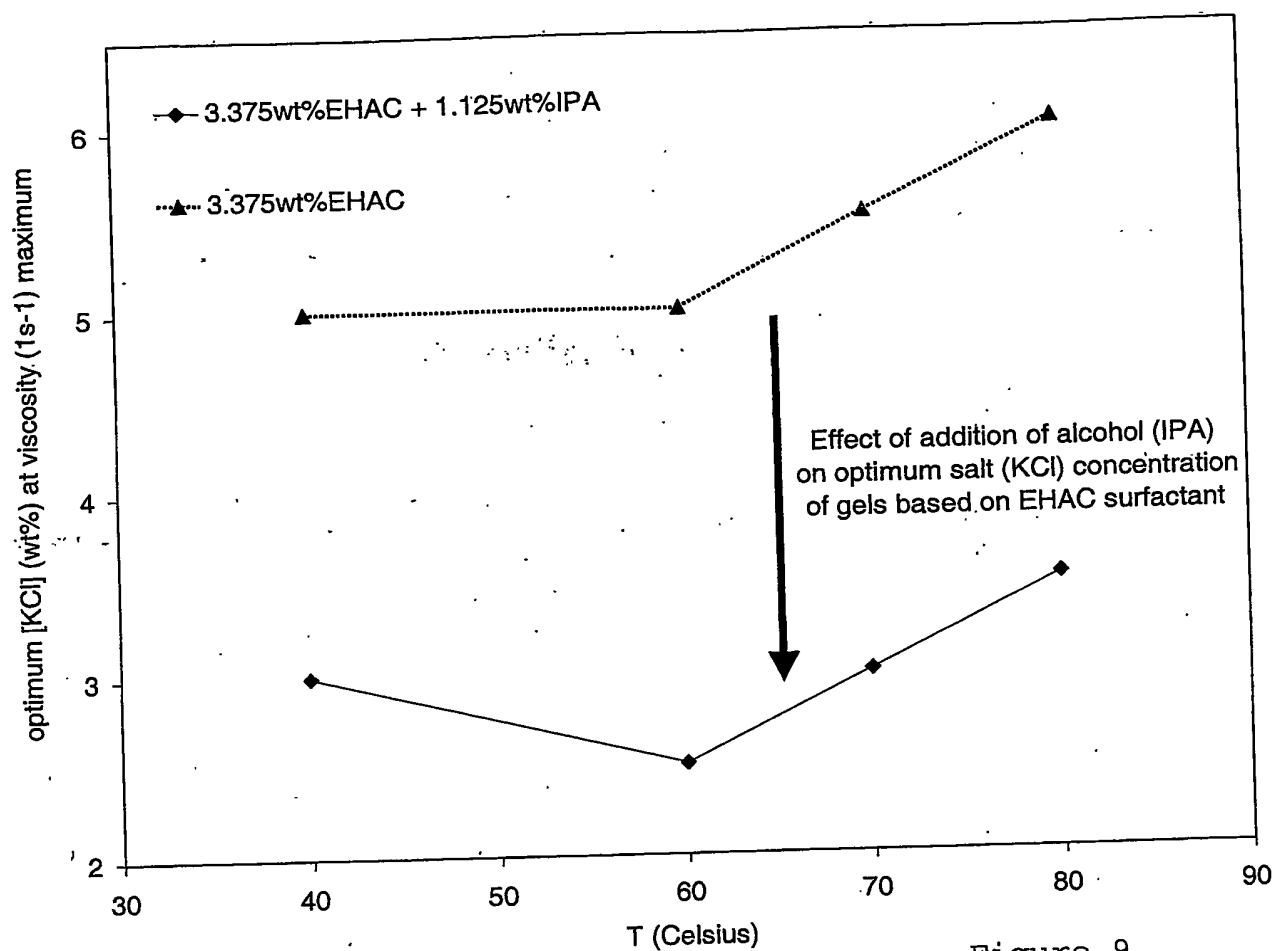


Figure 9

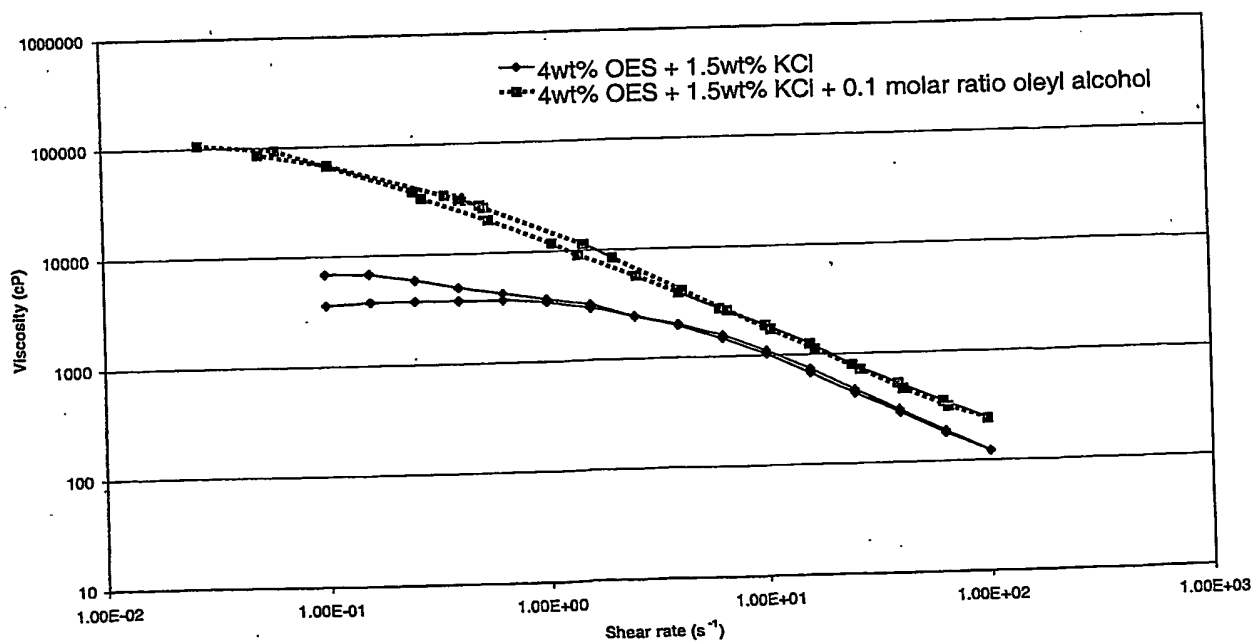


Figure 10

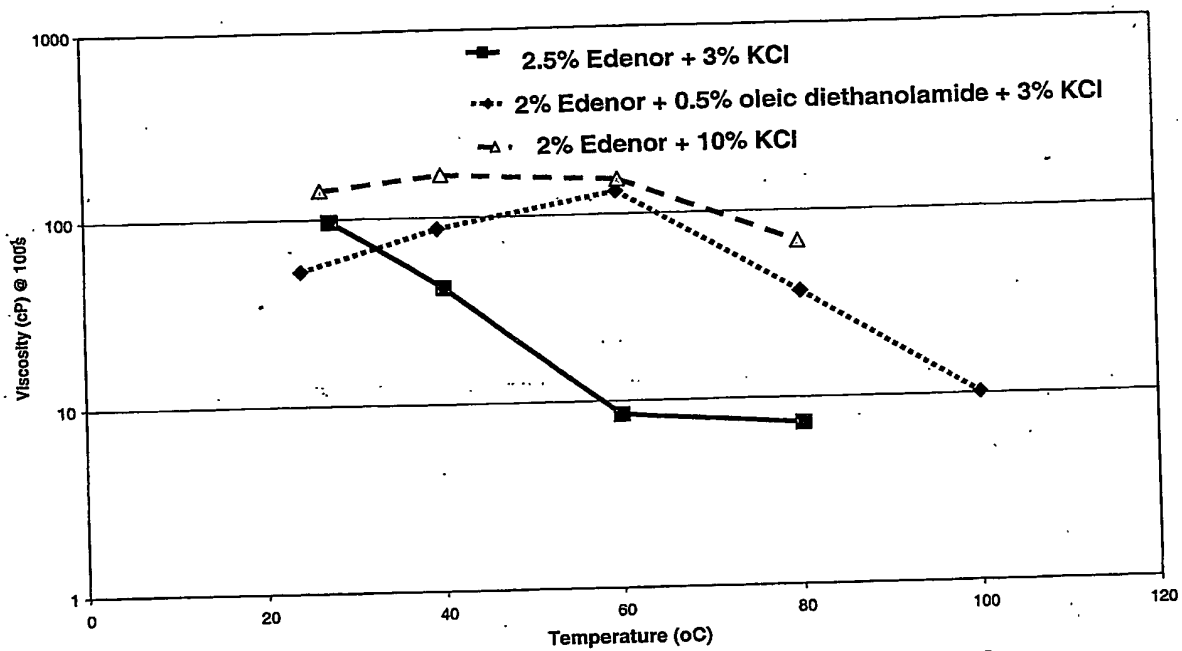


Figure 11

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